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# METHODS FOR CONVERSION OF CARBOHYDRATES IN IONIC LIQUIDS TO VALUE-ADDED CHEMICALS

## CROSS REFERENCE TO RELATED APPLICATION

This invention claims priority to Provisional application 60/836,188 filed Aug. 7, 2006; Provisional application 60/851,545 filed Oct. 13, 2006; and Provisional application 60/938,988 filed May 18, 2007 incorporated herein their entirety.

This invention was made with Government support under Contract DE-AC05-76RLO1830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

## FIELD OF THE INVENTION

The present invention relates to methods for conversion of carbohydrates in ionic liquids to value-added chemicals at substantial yields.

## BACKGROUND OF THE INVENTION

Replacing petroleum feedstocks with biomass feedstocks will require efficient methods for converting carbohydrates to a diverse number of chemical compounds. A major barrier to achieving this goal is a current inability to effectively utilize 5-carbon (C5) and 6-carbon (C6) carbohydrate building blocks derived from nature as potential feedstocks, including such abundant sugars as, e.g., glucose and fructose. 5-Hydroxymethylfurfural (HMF), an important versatile sugar derivative, is also considered a key intermediate between petroleum-based industrial organic chemistry and bio-based carbohydrate chemistry [Werpy et al. in "Top Value Added Chemicals from Biomass" United States Department of Energy report number DOE/GO-102004-1992; and Kamm et al. "Lignocellulose-based Chemical Products and Product Family Trees" in "Biorefineries-Industrial Processes and Products", 133 pp, Vol. 2 Edited by Kamm, B., Gruber, P. R. & Kamm, M, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006]. For example, HMF and its derivatives can potentially replace petroleum-based building blocks [Bicker et al. in *Green Chem.* 5, 280-284 (2003)] used to make plastics and fine chemicals. However, processes that produce pure HMF from abundant renewable carbohydrates as a basis for biorefinery platforms based on utilization of HMF must produce high yields and have low energy costs. For example, while HMF has been proposed as a key intermediate to produce liquid alkanes from renewable biomass resources [Leshkov et al., *Science* 312, 1933-1937 (2006)], high production costs currently limit availability and use of HMF industrially. Further, processes that produce HMF involve use of acid catalysts and are essentially limited to fructose as a feed material [Asghari et al., *Ind. Eng. Chem. Res.* 45, 2163-2173 (2006); Kuster et al., *STARCHE-STARKE* 42, 314-321 (1990); Leshkov et al., *Science* 312, 1933-1937 (2006); Tyrlik et al., *Carbohydr. Res.* 315, 268-272 (1999)]. FIG. 1 illustrates a conventional process for acid-catalyzed conversion of carbohydrates. In the figure, conversion of 6-carbon sugars employs concentrated acid (e.g., sulfuric acid) as a catalyst. Acids are corrosive, however, and have drawbacks including product contamination, and difficult recycling and waste disposal issues. Acids further catalyze side reactions leading to byproducts that require complicated product separations for product purification that increase costs. For example, in water

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under acidic conditions, HMF decomposes to levulinic acid and formic acid, making purification of HMF difficult. Challenges obtaining high yields of dehydration products from conversion of fructose are described, e.g., by Carlini et al. [Applied Catalysis A: General 275 (2004) 111-118].

When glucose is the feed material, HMF yields are usually low [Tyrlik et al., *Carbohydr. Res.* 315, 268-272 (1999); Watanabe et al., *Carbohydr. Res.* 340, 1925-1930 (2005)]. Under normal processing conditions, glucose fails to convert to HMF at high yields. Generally, glucose is poorly converted, presumably a consequence of competing reaction pathways that lead to formation of byproducts. With fructose, HMF yield is reported to increase in systems which partition HMF from H<sub>2</sub>O. For example, HMF yields increase in strong polar organic solvents such as dimethylsulfoxide (DMSO) as part of an aqueous-organic reaction medium [Leshkov et al., *Science* 312, 1933-1937 (2006)]. In another solvent system, HMF is reported to be formed from fructose in an ionic liquid solvent consisting of [BMIM]PF<sub>6</sub> or [BMIM]PF<sub>4</sub> with added co-solvent (e.g., DMSO) further including AMBERLYST-15®, an acidic polymer, as catalyst [Lansalot-Matras et al., *Catal. Commun.* 4, 517-520 (2003)]. In the absence of DMSO co-solvent, best yield of HMF is reported to be 40% to 52%. [Lansalot-Matras et al., *Catal. Commun.* 4, 517-520 (2003); and Moreau et al., *J. Mol. Catal. A: Chem.* 253, 165-169 (2006)]. In another system, a specialized ionic liquid, [HMIM]Cl is reported to act as a proton-transfer agent, or acid catalyst [Moreau et al., *J. Mol. Catal. A: Chem.* 253, 165-169 (2006)].

Polysaccharides (e.g., cellulose) are another class of carbohydrates that are a rich source of carbohydrate building blocks with both high conversion and high yield potential. However, polysaccharides typically require pretreatment to depolymerize the carbohydrates and provide necessary building blocks for conversion. Cellulose, for example, is presently pretreated with acid and subsequently converted to glucose via enzymatic hydrolysis. However, enzyme costs are high and complexity of processing leads to high capital costs. Alternatives such as acid hydrolysis produce by-products which are metabolic poisons to biological fermentation organisms, eliminating fermentation as a route to product conversion. Consequently, while carbohydrates can be converted through various processes including hydrolysis and biological fermentation, poisoning, slow processing, high production costs, and difficult separations result in high processing costs.

Accordingly, there remains a need for new processes that provide conversion of carbohydrates to value-added chemicals and chemical feedstock products at high conversion, high selectivity, and high yields.

## SUMMARY OF THE INVENTION

The invention relates to the use of ionic liquids for selective conversion of carbohydrates to value-added chemicals. In one method of the invention, selective conversion of a carbohydrate to value-added chemical(s) includes the steps of: mixing the carbohydrate up to a limit of solubility with an ionic liquid; heating the carbohydrate in the ionic liquid at a reaction temperature in the absence of added catalyst for a reaction time sufficient for conversion of the carbohydrate. Conversion of the carbohydrate produces furans at a substantial yield.

In various embodiments, preferred ionic liquids used as solvents for conversion of carbohydrates have a chemical formula: 1-R<sub>1</sub>-3-R<sub>2</sub>-imidazolium chloride ([R<sub>1</sub>R<sub>2</sub>IM]Cl), where R<sub>1</sub> and R<sub>2</sub> are alkyl groups of formula (C<sub>x</sub>H<sub>2x+1</sub>) where